

Phosphorus Pools, Alkaline Phosphatase Activity, and Phosphorus Limitation in Hypereutrophic Onondaga Lake¹

Susan D. Connors and Martin T. Auer

*Department of Civil and Environmental Engineering
Michigan Technological University
Houghton, MI 49931*

Steven W. Effler

*Upstate Freshwater Institute Inc.
P.O. Box 506
Syracuse, NY 13214*

ABSTRACT

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We examined seasonality in the phosphorus (P) physiology of the phytoplankton assemblage of culturally hypereutrophic Onondaga Lake, an urban system located in metropolitan Syracuse, NY. Four years of monitoring data for ambient dissolved and cellular phosphorus pools and phytoplankton biomass and one year of alkaline phosphatase activity (APA) assays supported the assessment. Kinetic approaches utilizing ambient dissolved and stored nutrient pools were evaluated for their utility in tracking nutrient limitation and gave evidence for luxury uptake of soluble reactive P (SRP) and utilization of the dissolved organic P (DOP) pool by the lake's phytoplankton. The high concentrations of phytoplankton biomass maintained annually from mid-to late summer were sustained in part by the DOP pool. Concentrations of SRP appear to be an inadequate representation of nutrient limitation in the lake. The cellular concentration of P, represented by the cell quota (Q , $\mu\text{g particulate P} / \mu\text{g chlorophyll}$), was generally lower when SRP was depleted. APA is a sensitive indicator of the utilization of DOP and the occurrence of nutrient limitation. The threshold Q value for inducement of APA in the lake is about $1 \mu\text{gPP} / \mu\text{gChl}^{-1}$. The onset of APA can be used to identify conditions of resource limitation where further reductions in nutrient availability may be expected to yield proportional improvements in water quality. A kinetic framework that relates growth rate to cellular nutrient concentration (Droop kinetics) is favored over one based on ambient dissolved nutrient concentrations (Monod kinetics) for quantifying nutrient limitation in Onondaga Lake.

Key Words: nutrients, phosphorus, eutrophication, alkaline phosphatase activity, cell quota, nutrient limitation, phytoplankton.

Phosphorus (P) is considered the nutrient most likely to limit algal growth in freshwater systems because it is generally in the shortest supply relative to the needs of algae (Hutchinson 1973; Welch, 1992). As a result of this nutrient's role in eutrophication, P management is a focus of many lake restoration programs (Cooke et al. 1993). Under conditions of nutrient saturation, i.e. in hypereutrophic systems, water quality conditions may be insensitive to initial efforts to reduce P inputs; greater sensitivity is characteristic of less nutrient-rich

environments (Auer and Canale, 1982). Decisions regarding the magnitude of loading reduction required to achieve specific water quality goals require a knowledge of the occurrence and extent of P limitation.

The relationship between algal growth and nutrient availability is often quantified through kinetic frameworks embodied in mechanistic water quality models (Chapra and Reckhow, 1983, Thomann and Mueller, 1987). Two kinetic approaches are commonly applied (Bowie et al. 1985). The first, based on Monod (1942) kinetics, relates growth rate to the external (dissolved) nutrient concentration:

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$$G(N) = \frac{P}{K_p + P} \quad (1)$$

in which $G(N)$ is the fraction of the maximum specific growth rate (range 0 to 1, 1 corresponds to nutrient saturation) achieved at a particular phosphorus concentration ($\text{mgP}\cdot\text{L}^{-1}$), and K_p is the half-saturation constant ($\text{mgP}\cdot\text{L}^{-1}$), a measure of the organism's efficiency in acquiring P. Phosphorus immediately available to algae is typically assumed to be equal to the concentration of the analyte soluble reactive P (SRP), however, other dissolved forms (e.g., nonreactive or organic P) can support growth (Berman 1970, Taft et al. 1977). The second approach relates growth rate to the internal (or stored) nutrient concentration, i.e. Droop (1968) kinetics:

$$G(N) = 1 - \frac{Q_0}{Q} \quad (2)$$

in which Q is the cell quota (mass P/unit biomass⁻¹), and Q_0 is the minimum cell quota, i.e., the internal P concentration at which growth ceases.

The Droop model accommodates the phenomenon of luxury uptake (variable stoichiometry), where P is acquired by algae and stored at levels well beyond the immediate demand for growth (Droop 1968, 1973, Auer and Canale, 1982, Auer et al. 1986). By drawing on internal stores, algae can grow at near maximum rates during periods of water column nutrient depletion (Auer et al. 1986). A model based on internal nutrient stores is conceptually satisfying because it provides a mechanistic treatment of the factor controlling growth. Such models have seen limited management application, however, because of their inherent complexity (Bowie et al. 1985). The simpler Monod model cannot accommodate the luxury uptake phenomenon. However, fixed stoichiometry models (Monod kinetics) may be appropriately applied where the rate of change in water column nutrient levels is slow relative to the rate of growth, i.e. where internal nutrient pools are in balance with the external environment and a "cellular equilibrium" is achieved (DiToro 1980).

The relationship between algal growth and nutrient availability for both the Droop and Monod models is well described by a rectangular hyperbola (Fig. 1). Values of K_p and Q_0 used to develop this figure are those of Auer et al. (1986). Most rigorously, P limitation is defined as that region of the P-growth response curve where $G(N) < 1$. Bannister (1974, 1979) recommended a criterion for the boundary of nutrient limitation/saturation as a nutrient (SRP) concentration equal to 100 times the K_p value, i.e. $G(N) = 0.99$ in Eq. 1. According to this definition, conditions of P limitation correspond to nearly the full range of the algal growth

response portrayed in Fig. 1. Water quality management programs seek to achieve a more substantial degree of P limitation, e.g., moving toward the "elbow" of the curves in Fig. 1, where nearly proportional decreases in growth are observed as nutrients become less available.

Soluble reactive P (SRP) is an imperfect representation of the external P pool available for algae uptake. This analyte includes ortho-P and the reactive fraction of the dissolved organic P (DOP) pool. The unreactive fraction of the DOP pool is parameterized as the difference between the concentrations of TDP (total dissolved P) and SRP, i.e. (TDP-SRP). DOP can be made available to plankton (algae and bacteria) through enzymatic hydrolysis (Currie et al., 1986; Healey and Hendzel 1979, Gage and Gorham 1985). Enzymes cleave ortho-P groups from large organic P molecules which are otherwise unavailable to algae (Bentzen et al. 1992). The most well-known of these enzymes are the alkaline phosphatases, which have been the subject of many studies (e.g., Fitzgerald and Nelson 1966, Francko 1983, Hantke and Melzer 1993, Jones 1971, Pick, 1987, Wetzel 1981). Alkaline phosphatase activity (APA) is

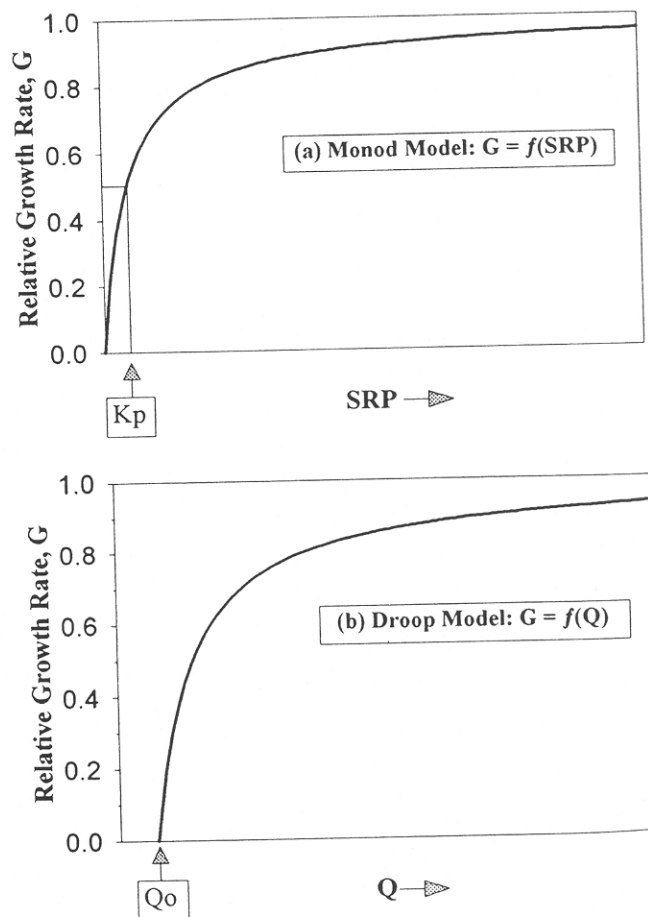


Figure 1.—Two models which describe the relationship between algal growth and P availability: a) Monod and b) Droop.

thought to play a major role in P regeneration in the water column (Ahn et al. 1993) and may serve to extend the duration of algal blooms in eutrophic lakes (Heath and Cooke 1975). Inverse relationships have been observed between APA and SRP concentration (Hernandez et al. 1992, Pettersson 1980, Reichardt 1971) and between APA and Q (Gage and Gorham 1985, Healy 1973, Wynne 1977), suggesting that APA is an indicator of P-deficient algae (Jansson et al. 1988).

Here we examine seasonality in the P physiology of the phytoplankton assemblage of a culturally hypereutrophic urban lake, as manifested in ambient dissolved and stored P supplies and APA. We evaluate the extent of P limitation experienced seasonally in the lake within the kinetic framework of the Monod (Eq. 1) and Droop (Eq. 2) models, demonstrating short-comings in the use of SRP, within the Monod framework, for quantification of the extent of P limitation in the test lake. In addition, we present evidence for the uptake of DOP by phytoplankton, following the depletion of SRP, and its interplay with APA. Finally, we establish relationships between APA, SRP and Q, and the utility of APA as an indicator of P limitation. This study provides guidance to lake managers and scientists in estimating the prevailing extent of P limitation and in selecting an appropriate quantitative framework to describe the relationship between P availability and algal growth. Further, it affirms the value of the APA assay as a tool supporting studies of the P cycle in productive waters.

Study System

Onondaga Lake is a polluted hypereutrophic system, located in metropolitan Syracuse, New York, which has received the municipal and industrial waste discharge of the region for over a century (Effler 1987). The lake has a surface area of 12.0 km², a volume of 1.31x10⁸ m³, a maximum depth of 20 m, and a mean depth of 12 m (Effler and Harnett 1996). Onondaga Lake flushes rapidly; e.g., an average of 3.9 times year⁻¹ over the 1971-1989 period, on a completely-mixed basis (Effler and Whitehead 1996). The third largest inflow is the discharge from the Metropolitan Syracuse Wastewater Treatment Plant (METRO); it represented 19% of the total inflow over the 1971-1989 period, and 25% of the inflow for the June-September interval for those years. Physical and chemical conditions in the lake are described by Effler et al. (1996a) and Perkins and Effler (1996).

Phosphorus is the nutrient limiting algal growth in Onondaga Lake: ratios of N/P (by weight) in the euphotic zone range from 29 to 290 (data of 1988-1990).

N/P ratios (by weight) > 13-16 indicate P limitation (Rhee 1978, Welch 1992). Historically, P loads to the lake were much greater than at present. The annual load of total P (TP) to the lake was reduced about 12 fold between the late 1960's and the late 1980's through a combination of management actions focusing largely on METRO; an approximately 20 fold reduction in the TP concentration of the facility's effluent was achieved over that same period (Effler and Whitehead 1996). The average TP concentration of the effluent since the late 1980's has been about 0.6 mgP·L⁻¹, substantially less than the limit of 1.0 mgP·L⁻¹ placed on dischargers within the Great Lakes Basin. METRO presently contributes 60-70% of the external TP load to Onondaga Lake (e.g., Effler and Whitehead 1996, Heidtke and Auer 1992).

Inputs and in-lake concentrations of P remain high today. Total P loads to the lake since the late 1980's have been about 250-300 kgP·d⁻¹ (Heidtke and Auer 1992; 21-25 mgP·m⁻²·d⁻¹), nearly 10 times the level identified by Vollenweider (1982) as excessive with respect to trophic state management. The summer average TP concentration for the upper waters over the interval 1989 - 1992 ranged from 65 to 93 µgP·L⁻¹, representative of extremely eutrophic conditions (Auer et al. 1986, Vollenweider 1982). Water quality manifestations of the lake's hypereutrophic state include excessive levels of phytoplankton and low clarity (Auer et al. 1990, Field and Effler 1983), severe summer hypolimnetic oxygen depletion (Effler et al. 1986a), and, during the fall turnover period, lake-wide depletion of oxygen (Effler et al. 1988) and coupled fish exodus (Ringler et al. 1996). Diversion of the METRO effluent to bypass the lake is a leading management alternative for remediating cultural eutrophication problems.

Methods

Weekly monitoring of the surface waters of Onondaga Lake (0 and 1m depth) during the summers of 1989 - 1992 was conducted at a centrally-located station in the south basin of the lake, found to be representative of lake-wide conditions (Effler 1996a). Phosphorus species (TP, TDP, and SRP) were analyzed spectrophotometrically using the ascorbic acid method of APHA (1989), with persulfate digestion for TP and TDP. Dissolved species were measured on the filtrate of samples passed through 0.45 µm cellulose acetate filters. The difference between the analytes TDP and SRP includes condensed and organic phosphates (APHA 1989) and is considered here as being representative of the DOP pool because of the magnitude of biological activity in the system and because the use of products

containing condensed P is controlled in the lake basin. Chlorophyll (Chl), determined according to the method of Parsons et al. (1984), was the measure of phytoplankton biomass. Cell quota, the P content per unit algal biomass, was estimated as the ratio of particulate P ($[PP] = [TP] - [TDP]$) to Chl, i.e. $\mu\text{gPP}\cdot\mu\text{gChl}^{-1}$. This expression of Q is imperfect to the extent that there are contributions to PP other than phytoplankton (bacteria and detritus; Welch, 1992) and that the cellular content of Chl is subject to variation (ratios of C:Chl vary by a factor of 4-10; Bowie et al., 1985). However the approach has been successfully applied previously in relating internal P stores and phytoplankton growth rates (Auer et al. 1986). Kinetic coefficients required for solution of the Monod and Droop models (K_p and Q_o in Eqs. 1 and 2) and the SRP- Q relationship introduced subsequently (k_q and $P_{t,q}$ in Eq. 3) are those determined for the natural phytoplankton assemblage of Green Bay, Lake Michigan by Auer et al. (1986). That study of nutrient and growth dynamics integrated the response of the natural assemblage over a broad trophic gradient for an entire growing season to develop representative kinetic coefficients. It is acknowledged that values for kinetic coefficients vary widely (cf. Bowie et al., 1985) and that coefficients specific to the phytoplankton assemblage of Onondaga Lake may differ somewhat from those reported for Green Bay and may vary seasonally. However, conditions of nutrient supply and algal biomass in Onondaga Lake are similar to those observed in the eutrophic portions of Green Bay and cell quota levels in the two systems are quite comparable. We believe that this analysis serves well in providing a comparative evaluation of the subject kinetic frameworks and in characterizing seasonal trends in P limitation.

In natural waters alkaline phosphatase enzymes act to hydrolyze a complex substrate (e.g., DOP), producing ortho-P and an organic by-product. The assay employed here is performed by adding an artificial substrate (3-o-methylfluoresceinphosphate, MFP) to a water sample. Upon hydrolysis, the substrate yields the readily detectable 3-o-methylfluorescein (MF). The substrate was prepared as 10 μM 3-o-methylfluoresceinphosphate (Sigma) in 10 mM Tris buffer (pH 8.5). Following addition of substrate, samples were incubated at 35°C in diffuse room light and MF concentrations were determined at 20 minute intervals over a two-hour period. MF was measured fluorometrically according to the method of Hill et al. (1968), as modified by Healy and Hendzel (1979), using a Turner Model 10 fluorometer equipped with a 47B primary filter and a No. 8 reference filter. APA was determined as the time rate of increase in MF per unit algal biomass ($\mu\text{molMF}\cdot\mu\text{gChl}^{-1}\cdot\text{hr}^{-1}$). Replicate assays were run periodically, yielding a variation of less than

5%. APA was measured over the June-August period of 1992.

Several researchers have found APA to be useful in identifying the occurrence of P deficiency in algae (Hantke and Melzer 1993, Heath and Cooke 1975, Smith and Kalff 1981) and have found APA to be related to other kinetically-based (e.g., Eqs. 1 and 2) indicators of P limitation (Gage and Gorham 1985, Pettersson 1980). Others have criticized APA. Jansson et al. (1988) indicated that the enzymes' affinity for natural substrates may vary depending on substrate structure and that the pH and temperature conditions maintained in the assay do not always correspond to those found in natural waters. Pick (1987) observed little short-term (18 hr) inhibition of enzyme activity following addition of ortho-P to P-deficient assemblages of natural phytoplankton.

Seasonality in P Pools and Phytoplankton Biomass

Observations of the seasonal distribution of dissolved P species, Q , and chlorophyll were made for 1989, 1990, 1991, and 1992 (Figs. 2, 3, 4, and 5, respectively). The pattern determined for APA in the summer of 1992 is included with the plot for Q (Fig. 5b). Despite year-to-year differences in the temporal details of these distributions, associated with interannual variations in the timing and intensity of phytoplankton blooms, several recurring patterns emerge (Figs. 2-5). Concentrations of DOP are initially high in spring (e.g., $\sim 50 \mu\text{gP}\cdot\text{L}^{-1}$, Figs. 2a, 3a, 4a, and 5a). SRP concentrations are high at the time of ice-out (usually early to mid-March). Major depletions in SRP, associated with the spring phytoplankton bloom (e.g., Figs. 2c, 3c, 4c, and 5c), are already manifested by the start of monitoring in April in 1990 (Fig. 3a), 1991 (Fig. 4a), and 1992 (Fig. 5a). An abrupt decrease in phytoplankton occurs annually in May or early June (Figs. 2c, 3c, 4c, and 5c) and has been described as a "clearing event" (Auer et al. 1990). Clearing events in Onondaga Lake have been attributed largely to zooplankton grazing, not to P-limitation (Auer et al. 1990, Siegfried et al. 1996). Note that while the timing of the clearing event in 1989 (Fig. 2) was apparently well matched by a major depletion in SRP, this was not the case in the other three years. DOP levels remained relatively high in all four years during periods in which clearing events occurred. This supports the view that reductions in algal biomass observed during clearing events are a manifestation of grazing pressure, not resource limitation.

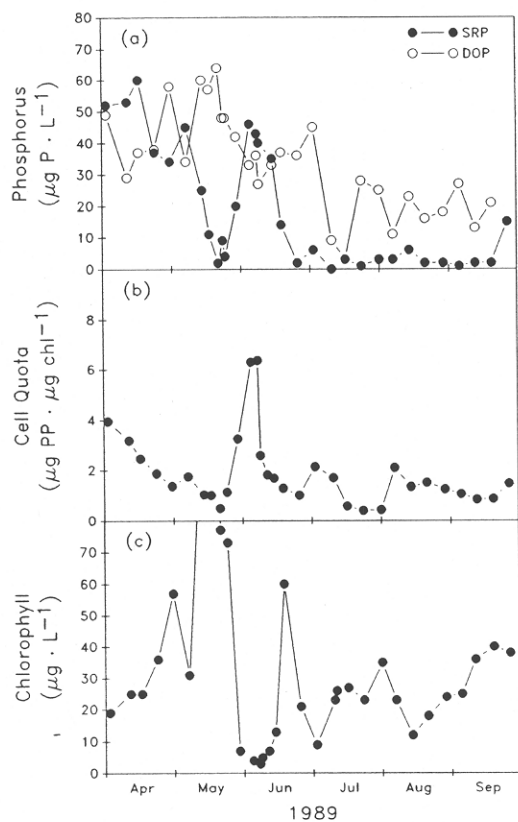


Figure 2.—Seasonality in: a) SRP and DOP, b) Q, and c) Chl for the upper waters of Onondaga Lake in 1989.

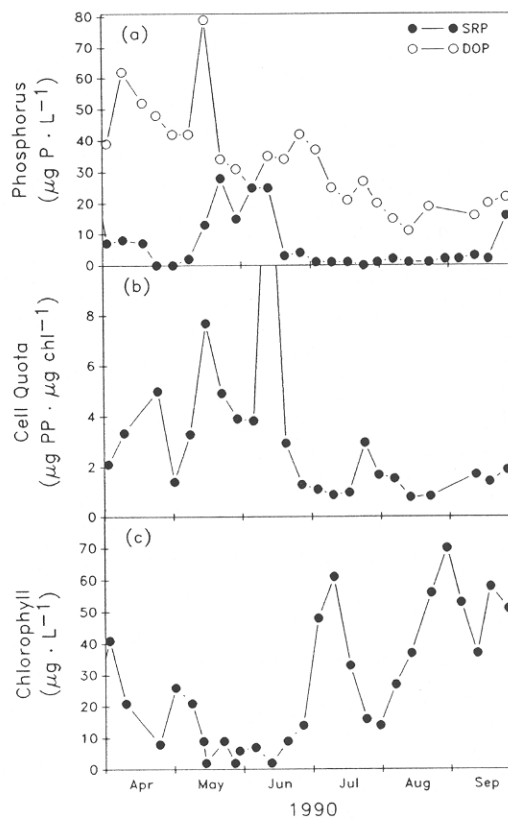


Figure 3.—Seasonality in: a) SRP and DOP, b) Q, and c) Chl for the upper waters of Onondaga Lake in 1990.

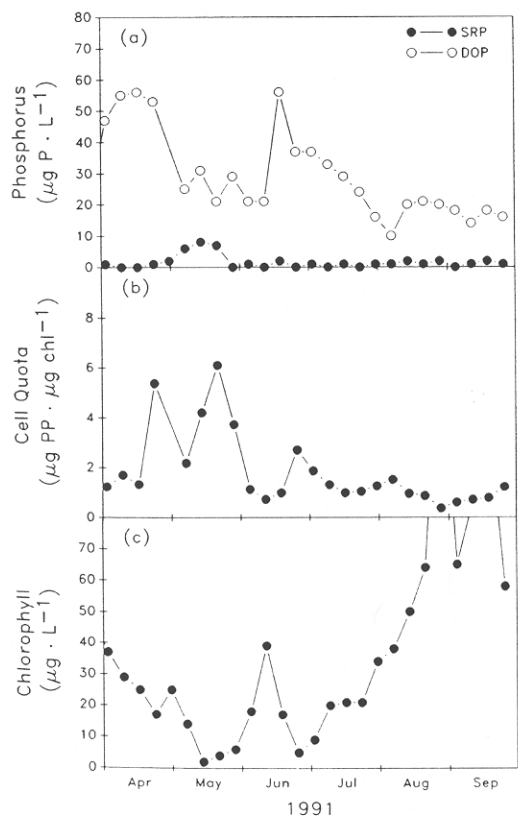


Figure 4.—Seasonality in: a) SRP and DOP, b) Q, and c) Chl for the upper waters of Onondaga Lake in 1991.

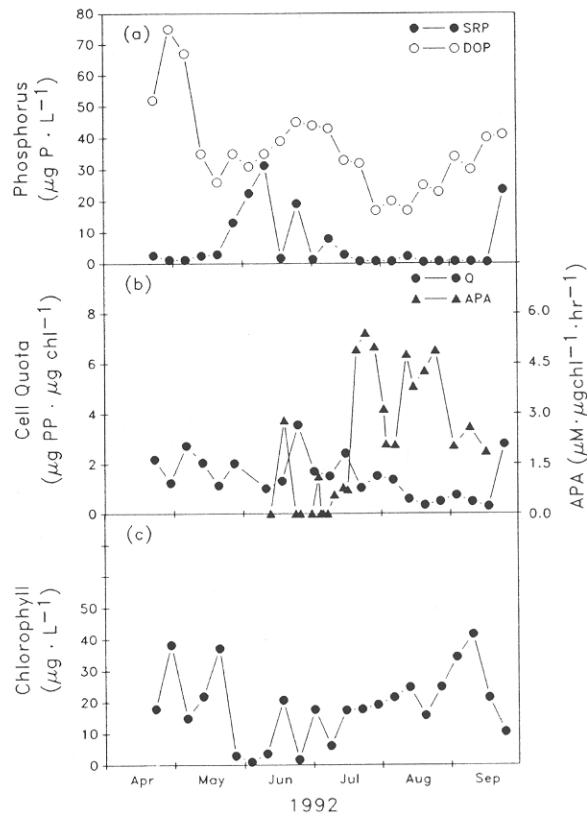


Figure 5.—Seasonality in: a) SRP and DOP, b) Q and APA, and c) Chl for the upper waters of Onondaga Lake in 1992.

Abrupt increases in SRP are quite evident during the clearing events (Figs. 2a, 3a, 4a, and 5a). These increases presumably reflect a reduction in phytoplankton uptake, with continued external loading, and perhaps rapid recycling of P within the upper waters (Lehman 1980, Auer et al. 1990). The cellular P content (Q) of the remaining standing crop apparently increases during clearing events (Figs. 2b, 3b, 4b, and 5b), consistent with the phenomenon of luxury uptake. The possible role of a larger relative contribution to the PP pool from non-phytoplankton components cannot, however, be discounted. Distinct blooms occur following clearing events in this high nutrient, high light environment in three of the four years.

Phytoplankton biomass remains relatively high from mid- to late summer (Figs. 2c, 3c, 4c, and 5c). Periods of decline are generally not as dramatic or as long as during the clearing events. SRP concentrations remain relatively low (mostly $< 2 \mu\text{gP}\cdot\text{L}^{-1}$) during this period, as do the values of Q (mostly $< 2 \mu\text{gPP}\cdot\mu\text{gChl}^{-1}$). The DOP pool decreases over this period of depleted SRP, suggesting algal utilization to sustain the elevated levels of phytoplankton biomass. Clear indications of uptake from the DOP pool are also seen during the spring blooms of 1991 (Fig. 4a) and 1992 (Fig. 5a). Several researchers have indicated that both SRP and DOP can be utilized by algae (Bentzen et al. 1992, Cotner and Wetzel 1992, Pick 1987). The leveling off or increase in DOP in late summer and early fall may reflect inputs of SRP and DOP originating through entrainment of P-rich hypolimnetic water (e.g., Effler et al. 1986b), depletion of the labile portion of the DOP pool, and/or reduced demand as the environmental conditions supporting phytoplankton growth (e.g., light and temperature) become less favorable.

The APA pattern in 1992 (Fig. 5b) provides more compelling evidence of the utilization of the DOP pool by the phytoplankton assemblage of Onondaga lake. The pattern complements the temporal details of the distributions of the dissolved fractions. APA increases in mid-July with the onset of low SRP concentrations, and DOP concentrations decrease, consistent with increased enzyme activity and subsequent uptake of cleaved ortho-P. The lower Q levels maintained in late summer, when the DOP pool is being utilized, suggest that the kinetics of uptake for this pool are less favorable than for SRP. This is consistent with the energetics of the process, as DOP utilization requires the extra step of hydrolysis prior to uptake. The increase in the DOP pool in September parallels the decrease in APA (Fig. 5a and b). Ahn et al. (1993) reported a similar seasonality in APA in Lake Soyang, Korea: activity was low in spring and increased over the summer. High levels of APA were attributed to a shortage of ambient inorganic P and low stored P reserves (Ahn et al. 1993).

Estimates of the Extent of P Limitation

Temporal distributions of $G(N)$ were calculated according to both the Monod and Droop expressions for each of the four years, 1989-1992 (Figs. 6a-6d). Kinetic coefficients required for the calculation of $G(N)$ (Eqs. 1 and 2; $K_p = 0.9 \mu\text{gP}\cdot\text{L}^{-1}$ and $Q_o = 1.4$

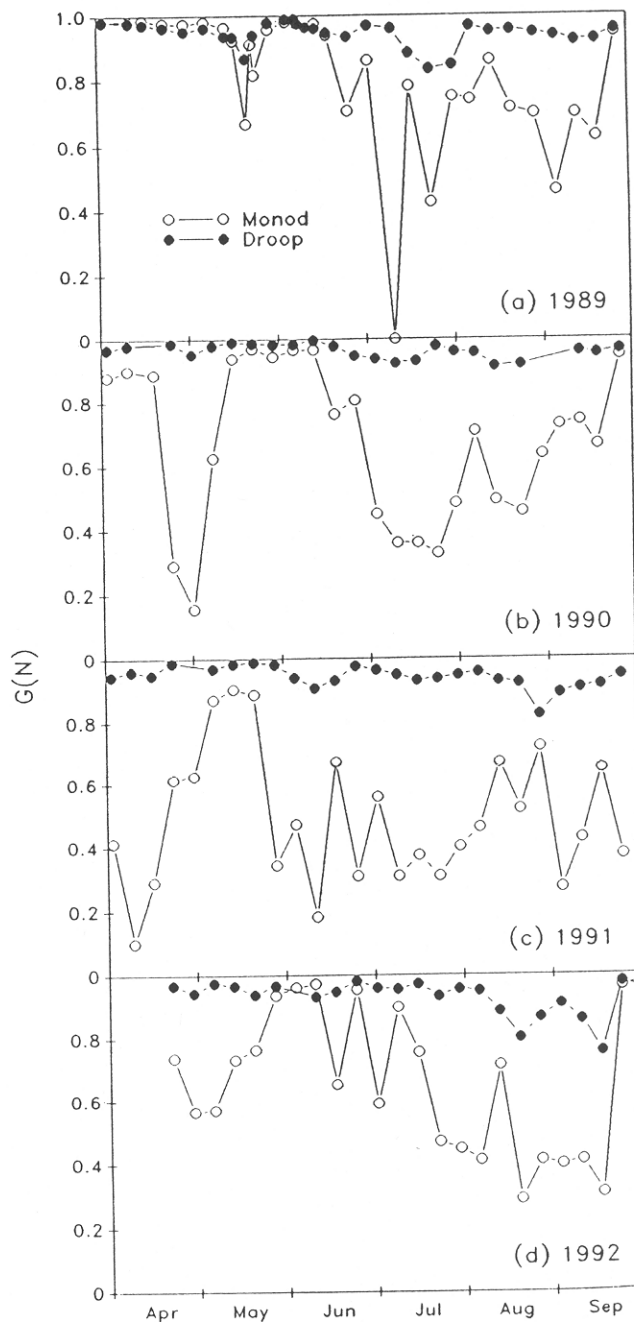


Figure 6.—Temporal distributions of estimates of nutrient limitation ($G(N)$) of phytoplankton growth in Onondaga Lake according to the Monod and Droop expressions: a) 1989, b) 1990, c) 1991, and d) 1992.

$\mu\text{gPP}\cdot\text{mgPOC}^{-1}$) are those of Auer et al. (1986). The value of Q_0 has been converted to be consistent with the units of biomass employed here ($Q_0 = 0.067 \mu\text{gPP}\cdot\mu\text{gChl}^{-1}$) based on the POC/Chl ratio observed for Onondaga Lake ($0.048 \text{ mgPOC}\cdot\mu\text{gChl}^{-1}$; unpublished data from S.W. Effler). The Monod framework depicts a much greater degree of limitation annually than the Droop model (Fig. 6) and implies a strong seasonality in $G(N)$ which is inconsistent with the dynamics of the phytoplankton standing crop (Figs. 2c, 3c, 4c, and 5c) and with measures of the flux of algal biomass from the epilimnion (Effler 1996b). For example, the Monod model predicts low values of $G(N)$ during extended periods of high Chl. Further, the downward fluxes of Chl and POC (measures of primary production, data of Effler 1996b), remain high through the period of low SRP in the summer of 1989, consistent with conditions of near nutrient-saturated growth. It is noteworthy that the value of K_p adopted for these calculations is near the lower end of the range commonly used in phytoplankton models (Bowie et al. 1985). Even greater degrees of limitation would be predicted by the Monod model if values at the upper end of the range were applied. Less information is available on ranges for Q_0 , however, sensitivity analyses indicate that these conclusions remain valid for values of Q_0 more than two times that employed here.

The inadequacy of the Monod model and SRP in representing the status of P limitation in the phytoplankton of Onondaga Lake as developed above (Fig. 6) is further supported by the temporal dynamics of the various P pools (Figs. 2-5). There is strong evidence that SRP is not the sole P-source, i.e. DOP is utilized. Thus algal growth is not mediated by water column SRP levels as implied by Monod kinetics. Further, the Monod model is of limited utility where the assumptions of "cellular equilibrium" (DiToro 1980) are not met. The $G(N)$ distributions which emerge from application of the Droop framework, based instead on the internal nutrient status of the phytoplankton, are by comparison more realistic (Fig. 6). Internal P concentrations are sufficient to sustain near maximum rates of algal growth over the entire spring to early fall interval, even when SRP becomes depleted (Fig. 6). Accordingly, the Droop model suggests that P limitation does commonly occur in Onondaga Lake over the spring-fall interval, but that the degree of limitation is quite small.

Relationships Between APA and Other Indicators of P Limitation

The response of APA to changes in SRP and Q in Onondaga Lake (Fig. 7) indicates that APA is a strong function of SRP. The shape of the curve (Fig. 7a) suggests initiation of APA at an SRP concentration of about $1\text{--}2 \mu\text{gP}\cdot\text{L}^{-1}$, with marked suppression above $2 \mu\text{gP}\cdot\text{L}^{-1}$. These findings are consistent with those of Pettersson (1980) where APA was observed to increase at ortho-P concentrations $< 1 \mu\text{gP}\cdot\text{L}^{-1}$.

APA is clearly related to Q as well and is apparently initiated in response to a reduction in the internal P reserves of the algae (Fig. 7b). The inflection point (Fig. 7b) suggests initiation of APA at a Q value of about $1 \mu\text{gPP}\cdot\mu\text{gChl}^{-1}$. Gage and Gorham (1985) and Pettersson (1980) noted a similar inflection in the APA - Q relationship, however, a direct comparison of their results with those presented here is not possible due to differences in the units of expression of Q . Gage and Gorham (1985) proposed that the inflection point be utilized as a warning level for incipient P starvation.

The relationship between APA and Q should be considered more fundamental than that between APA and SRP, consistent with concepts of nutrient limitation which propose that the stored nutrient pool size regulates growth (e.g., Auer and Canale 1982, Droop 1968, 1973). Wynne (1981) reported that phosphatases

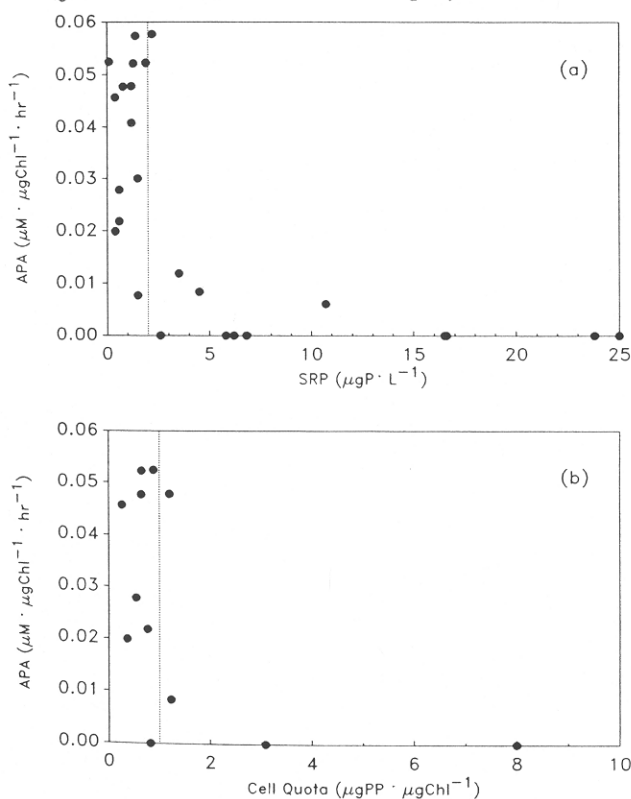


Figure 7.—Relationships between APA and: a) SRP, and b) Q , for the surface waters of Onondaga Lake. Lines indicate the apparent onset of suppression of APA.

in Lake Kinneret were controlled by changes in stored P and/or by other metabolic processes, rather than by ambient dissolved P concentrations. This was also recognized by Gage and Gorham (1985) for Minnesota lakes where reductions in APA were used to define the point at which cells began to accumulate surplus cellular P.

The relationship between APA and SRP is, by comparison, an indirect or second generation effect (Pettersson 1980, Pick 1987). Ambient dissolved nutrient levels determine the stored nutrient pool size and pool size governs APA. The strength of the APA - SRP relationship is dictated by the degree to which SRP and Q match up in real time, i.e. whether or not cellular equilibrium is achieved (cf. DiToro 1980). Equation 3 describes the relationship between SRP (P) and cell quota (Q) as derived by Auer et al., 1986:

$$Q = Q_o + Q_{s,max} \cdot \left[\frac{P - P_{t,Q}}{(k_Q - P_{t,Q}) - (P - P_{t,Q})} \right] \quad (3)$$

where $Q_{s,max}$ is the maximum surplus cell quota ($\mu\text{gPP}\cdot\mu\text{gChl}^{-1}$), i.e. the maximum amount which may be accumulated in excess of Q_o , $P_{t,Q}$ is the SRP threshold for accumulation of surplus cell quota ($\mu\text{gP}\cdot\text{L}^{-1}$), and k_Q is the SRP half-saturation constant for accumulation of surplus cell quota ($\mu\text{gP}\cdot\text{L}^{-1}$). This function is fit to field data for Onondaga Lake (Fig. 8), utilizing values of Q_o ($0.067 \mu\text{gPP}\cdot\mu\text{gChl}^{-1}$) and k_Q ($1.4 \mu\text{gP}\cdot\text{L}^{-1}$) as derived by Auer et al. (1986) and yielding values of $Q_{s,max} = 3 \mu\text{gPP}\cdot\mu\text{gChl}^{-1}$ and $P_{t,Q} = 0.4 \mu\text{gP}\cdot\text{L}^{-1}$.

In cases where SRP concentrations achieve some stability (Fig. 8a; the 1992 data subset), cellular equilibrium can be approached and the functionality relating SRP and Q is apparent. But when examined over a larger time frame (Fig. 8b; the entire 1989-92 data set), a greater number of outliers is observed and the relationship between SRP and Q is less clear. The SRP - APA relationship suffers as well. It is the presence of outliers and the frequency of their occurrence in systems with dynamic nutrient environments, which make SRP a poor indicator of nutrient limitation. For water quality managers, the APA analyte may offer the best information on conditions of resource limitation. Engendered in response to reduced internal nutrient pool size and attendant reductions in growth rate, the onset of APA signals incipient nutrient stress. The onset of APA (i.e., the inflection points in Figs. 7a, 1-2 $\mu\text{gSRP}\cdot\text{L}^{-1}$, and 7b, 1 $\mu\text{gPP}\cdot\mu\text{gChl}^{-1}$) were identified within the context of Monod and Droop kinetics (Figs. 9a-9c). Kinetic coefficients supporting these calculations are as presented previously (see Figs. 6 and 8). Moving to the left in Figs. 9a-c, away from conditions of nutrient saturation, it can be seen that the onset of APA occurs:

- where the growth response described by the

Monod model becomes linear with respect to SRP (Fig. 9a);

- where the rate of accumulation of cell quota becomes linear with respect to SRP (Fig. 9b); and
- as the elbow of the growth response described by the Droop model is approached (Fig. 9c).

In each case, further reductions in nutrient availability may be expected to yield proportional reductions in algal growth. We believe that this is a criterion for nutrient limitation which is of value to water quality managers and which may be assayed with some degree of confidence. Perhaps one could go further, identifying subsets of data where extended periods of low and stable SRP, reduced Q and increased APA permit one to place the system more specifically within and along the linear region of the response curve. However, complications associated with all three measures of nutrient limitation introduce uncertainty to the analysis and make such conclusions unreliable.

Applied here as a basis for assessing nutrient limitation in Onondaga Lake, these relationships (Fig. 9) would suggest that a modest level of limitation (~75-90% of the maximum specific growth rate) is achieved only in late summer and that the degree of

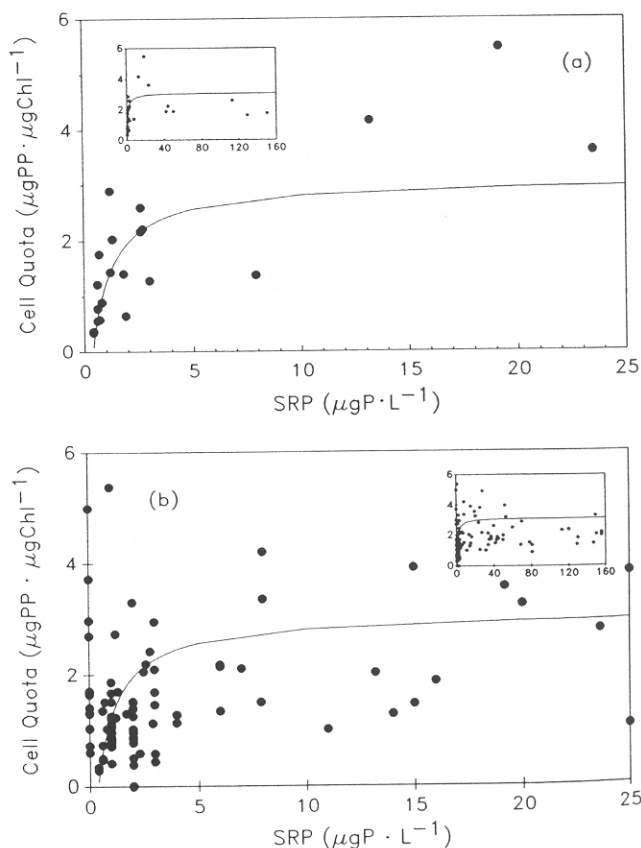


Figure 8.—Relationship between Q and SRP in the surface waters of Onondaga Lake: a) subset of data for 1992 and b) entire data set, 1989-92. Insets expand the range of observations.

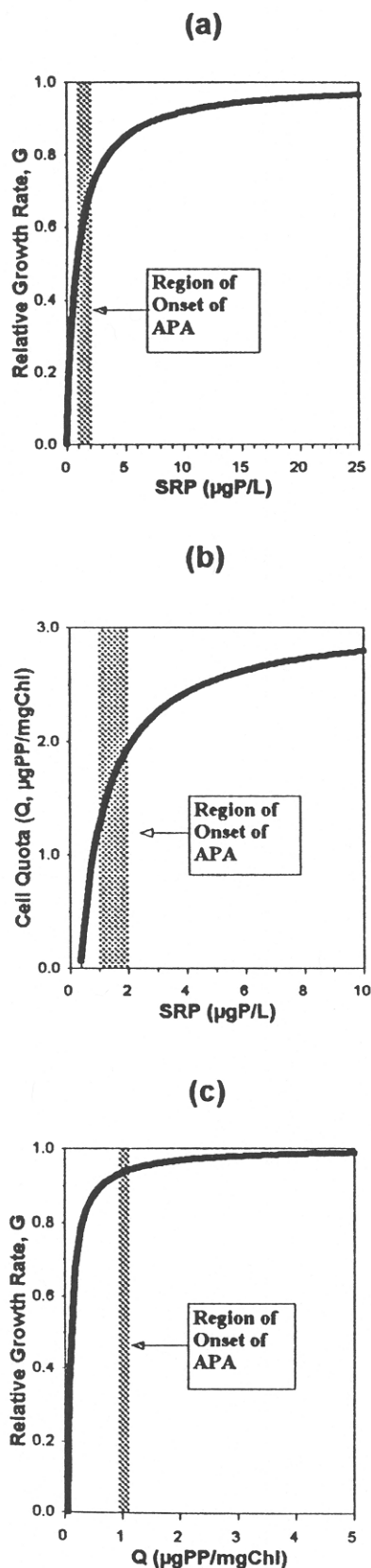


Figure 9.—Onset of APA (shaded region) as related to: a) growth rate, Monod kinetics, (b) accumulation of internal nutrient stores, and c) growth rate, Droop kinetics.

limitation in late summer has increased over the study period (1989-92, Fig. 6). Undoubtedly the availability of P to phytoplankton in Onondaga Lake was greater in the 1960's and 1970's, e.g. higher concentrations of dissolved and stored P and more nearly saturated growth. Major reductions in loading from METRO since the late 1960's have altered the nutrient status of the lake, moving the system from conditions of saturation and near-saturation toward a small degree of nutrient limitation. This is consistent with observations that only slight changes in related water quality characteristics (algal standing crop, transparency, oxygen resources) have occurred over the period of loading reductions. Apparently further reductions in P loading to Onondaga Lake will be necessary to achieve a substantial degree of nutrient limitation (e.g. an approach to the near linear portions of the curves in Fig. 1) with related water quality benefits.

Summary

Recurring linked patterns in the dynamics of ambient dissolved and internal P pools and phytoplankton biomass emerge from the analysis of monitoring data for the spring to early fall interval of four consecutive years in Onondaga lake. Luxury uptake of P by phytoplankton during periods of high SRP concentrations, particularly during clearing events, is reflected by increases in Q . Annual depletions in the DOP pool, coincident with increases in APA, occur during the mid- to late summer interval when SRP concentrations are low, providing compelling evidence for the utilization of DOP by the lake's phytoplankton assemblage. The high phytoplankton biomass maintained over this interval is apparently sustained, at least in part, by the DOP pool. Levels of Q are lower over this period suggesting that DOP uptake kinetics are less favorable than those for SRP.

A kinetic framework which relates algal growth to internal nutrient pool size (e.g. Droop kinetics) is favored over an approach based on ambient dissolved nutrient levels (e.g. Monod kinetics). SRP data provide an inadequate representation of the status of P limitation of phytoplankton in Onondaga Lake, and undoubtedly other dynamic, productive lakes, because of the availability of DOP as an alternative P source and because growth can be sustained by stored P, apparently uncoupled from ambient conditions in the dissolved environment, i.e. cellular equilibrium is not maintained. APA is a more appropriate indicator of nutrient availability, signaling the utilization of DOP and providing a criterion for the initiation of nutrient

limitation consistent with goals for water quality management. The threshold Q value for onset of APA in Onondaga Lake is $1 \mu\text{gPP}\cdot\mu\text{gChl}^{-1}$. Below this level, proportional reductions in algal growth and associated water quality conditions may be anticipated in response to reductions in nutrient availability. By this criterion, algal growth in Onondaga Lake is nutrient limited only in late summer and then only to a small degree. Additional external loading reductions will be required to bring the system into the linear region of the growth - response curve.

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